# APPARATUS AND METHOD FOR LOW TEMPERATURE STRIPPING OF PHOTORESIST AND RESIDUES

#### **Related Application**

The present application claims priority from U.S. Provisional Patent Application Serial No. 60/430,002, filed November 29, 2002, bearing the same title, and is incorporated herein by reference in its entirety.

## **Background of the Invention**

- The present invention is related generally to the field of processing using photoresist and, more particularly, to a highly advantageous apparatus and associated method for accomplishing low temperature removal of photoresist and residues.
- Currently, most systems for photoresist removal (stripping) from semiconductor substrates use plasma sources for generating oxygen atoms to remove the photoresist (organic polymer) by oxidation at a substrate temperature of 150 Celsius to 300 Celsius. Such systems currently remove photoresist at high rates typically above a micron per minute of processing. This allows the systems to be commercially efficient in cleaning many substrates such as wafers per hour of processing. More recently, other gases have also been used either as additives to oxygen, or as the principal injected gas. These gases may improve stripping rate or permit inorganic or other residues, remaining after the bulk of the photoresist polymer, to be more efficiently and converted to volatile species or to soluble compounds that can be washed off of the surface. Recently, stripping, in some circumstances, has used gas mixtures that utilize hydrogen as the source of reactive species, rather than oxygen. Hydrogen atoms react with organic polymers to produce mostly volatile hydrocarbons and some other species containing oxygen. In these processes, the substrate temperature also must be maintained above about 150 Celsius for acceptable stripping rates to be achieved.
- The typical photoresist layer to be removed is an organic polymer that has already been used as a mask to pattern or implant the surface of the substrate. Oxygen mixed with varying amounts of other gases, including hydrogen and/or hydrogen containing molecules, and/or gases that contain fluorine, is typically injected into the plasma source that produces the reactive species/radicals that react with the photoresist. During photoresist stripping, the photoresist bearing surface of the substrate is exposed to the reactive radicals and the bulk of the organic material is removed. Such radicals may include oxygen atoms, hydrogen atoms, fluorine atoms, hydroxyl radicals and others. The surface is also exposed to the reaction products produced by the reaction of such radicals with the photoresist layer. The reaction products are mostly volatile species such as carbon oxides and water vapor or hydroxyl radicals and the reaction products as well as unused process reactants to be pumped out of the chamber. A large portion of the bare surface of the substrate is exposed to all these species during the stripping process, and the remaining areas are exposed as the photoresist layer is being removed.
- Most of these radicals are capable of reacting at higher temperatures with the sensitive materials found on the surface of the semiconductor substrates such as silicon wafers, during transistor fabrication. In some cases, the sensitive materials include some dielectric materials which will be used for the gate insulator of the transistors. In other cases, the bare silicon surface may be exposed or silicon with a very thin "native" silicon dioxide layer covering it. These sensitive

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surfaces and materials need to be very well controlled in all their properties for the transistors to have desired characteristics and reliability. The dielectrics likely to be used for the next decade in IC fabrication on silicon include silicon oxynitride, silicon nitride, and metallic oxides, oxy-nitrides and silicates that may have some nitrogen content (the latter being known as "high-k" dielectric materials). These dielectric materials can be composed of a single layer or they can be formed from two or more laminated or blended layers. These sensitive dielectric materials are known to be affected by exposure to oxygen atoms, hydrogen atoms, hydroxyl radicals or fluorine atoms at elevated temperatures. It is also the case that any such dielectric material will be damaged by the accumulation of a certain concentration of electric charge on the surface – which may be unavoidable if the radicals are produced by a plasma source. Therefore, current systems employed for stripping the photoresist (plasma based) may cause damage – both chemical and electrical - to either crystalline silicon or the sensitive dielectrics that will be used for transistors in the near future. This presents IC manufacturers with a potential problem in not being able to strip photoresist without damaging the exposed or underlying sensitive surfaces of the semiconductor substrate, reducing the yield or reliability of the ICs that are fabricated thereon.

- Further, new photoresist polymers that have heavily fluorinated backbone polymers will be coming soon to IC fabrication. These will first come to only the finest feature patterning processes, but within a few years will be used for a number of steps. Some substantial fraction of this fluorine is liberated as atoms from the polymer as it is stripped with oxygen atoms. The fluorine atoms can then also cause damage to the thin and sensitive gate dielectrics that will be used in the near future. This fluorine can even damage gate dielectrics that are covered by a thin gate electrode material such as polysilicon or other protective layer such as amorphous silicon.
- For the next several years, it is likely that silicon oxy-nitride will be the predominant material used for gate dielectric, but in the near future the new high-k dielectrics will become dominant. These materials are chemically sensitive to radicals, particularly at higher temperature. In particular, fluorine, oxygen and hydrogen atoms are all known to cause damage to such dielectrics and most cause chemical alteration or roughening of a silicon surface depending on the substrate temperature. Therefore, the present invention provides a highly advantageous and heretofore unseen method and associated apparatus for stripping photoresist, under the aforedescribed conditions, efficiently and rapidly, while avoiding damage to sensitive dielectrics or other surfaces on semiconductor substrates.

#### **Summary of the Invention**

As will be discussed in more detail hereinafter, there is disclosed herein a system and associated method for use in removal of process related materials from at least one substrate. Accordingly, in one aspect of the present invention, the substrate is supported in a processing chamber and means is provided for exhausting gases from the processing chamber. A source of reactive gas phase radicals is located outside of the processing chamber. The reactive gas phase radicals are conveyed from the source to the processing chamber for communication with the substrate therein. At least one surface of the substrate is exposed to ultraviolet radiation to illuminate the substrate surface such that the ultraviolet radiation activates reactions between the gas phase radicals and the process related materials for use in removal of the process related materials.

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- In another aspect of the present invention, a system and associated method are disclosed for use in removal of process related materials from at least one substrate. The substrate is supported in a processing chamber and means is provided for exhausting gases from the processing chamber. A first source generates at least a first species of reactive gas phase radicals, outside of the processing chamber. A second source, outside of the processing chamber, generates at least one of a selected gas and a second species of reactive gas phase radicals. The first species of reactive gas phase radicals from the first source and provided ones of the selected gas and the second species of reactive gas phase radicals, from the second source, are conveyed to the processing chamber for reaction therein for use in removing the process related materials.
- In still another aspect of the present invention, a system and associated method are disclosed for use in removal of process related materials from at least one substrate. The substrate is supported in a processing chamber and means is provided for exhausting gases from the processing chamber. A source of reactive gas phase radicals is located outside of the processing chamber. The reactive gas phase radicals are conveyed from the source to the processing chamber for communication with the substrate therein. A source of ultraviolet radiation is situated to expose the reactive gas phase radicals to an ultraviolet radiation prior to reaching the substrate such that the ultraviolet radiation energizes the reactive gas phase radicals to thereafter activate reactions between the gas phase radicals and the process related materials for use in removal of the process related materials without directly exposing the substrate to the ultraviolet radiation.

### **Brief Descriptions of the Figures**

- ¶11 The present invention may be understood by reference to the following detailed description, taken in conjunction with the drawings briefly described below.
- ¶12 FIGURE 1 is a diagrammatic view, in elevation, illustrating one embodiment of a system, produced in accordance with the present invention, for use in removing photoresist and associated residues from a substrate in which the substrate is exposed to UV energy in conjunction with a reactive species which is produced external to the processing chamber.
- ¶13 FIGURE 2 is a diagrammatic view, in elevation, illustrating another embodiment of a system, produced in accordance with the present invention, for use in removing photoresist and associated residues from a substrate in which the substrate is exposed to first and second reactive species, each of which is generated external to the processing chamber while, at the same time, the substrate and reactive species are exposed to UV energy.
- ¶14 FIGURE 3 is a diagrammatic view, in elevation, illustrating still another embodiment of a system, produced in accordance with the present invention, for use in removing photoresist and associated residues from a substrate in which externally generated first and second reactive species are exposed to one another prior to entering the processing chamber for exposure of the substrate thereto, as well as exposure of the substrate and mixture of first and second radical species to UV energy.
- ¶15 FIGURE 4a is a diagrammatic view, in elevation, illustrating a first modified form of the system and method of Figure 1, produced in accordance with the present invention, in which a window is positioned so as to eliminate certain UV photons.

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- ¶16 FIGURE 4b is a diagrammatic view, in elevation, illustrating a second modified form of the system and method of Figure 1, produced in accordance with the present invention, in which a UV transparent showerhead type dispersion plate is positioned above the substrate and below the UV energy source and an inlet of the reactive species.
- FIGURE 4c is a diagrammatic view, in elevation, illustrating a third modified form of the system and method of Figure 1, produced in accordance with the present invention, in which a UV window is positioned, for example, to eliminate UV photons with energies sufficiently high so as to cause damage to sensitive materials on the substrate or to promote additional activation of radical species. Further, a UV transparent showerhead type dispersion plate is positioned above the substrate as well as below the UV energy source and the inlet of the reactive species.
- ¶18 FIGURE 4d is a diagrammatic view, in elevation, illustrating a modified form of the system of Figure 4c, produced in accordance with the present invention, in which the dispersion plate further serves to eliminate UV photons from reaching the substrate.
- ¶19 FIGURE 4e is a diagrammatic view, in elevation, illustrating a modified form of the system of Figure 4d, produced in accordance with the present invention, in which a two-piece diversion plate arrangement is used wherein apertures defined by one diversion plate are offset with respect to apertures defined by the other diversion plate.

# **Detailed Description of the Invention**

- The following description is presented to enable one of ordinary skill in the art to make and use the invention and is provided in the context of a patent application and its requirements. Various modifications to the described embodiments will be readily apparent to those skilled in the art and the generic principles herein may be applied to other embodiments. Thus, the present invention is not intended to be limited to the embodiment shown but is to be accorded the widest scope consistent with the principles and features described herein.
- This system for dry cleaning of substrates uses ultraviolet light and/or chemical energy, instead of high substrate temperatures, to activate chemical reactions between reactive radicals from one or more separated sources, and photoresist and/or the residues left after at least partial photoresist removal. Reactive species, radicals and/or gases may be provided to the processing chamber from one or more separate sources. Such reactive species source(s) may employ plasma or may use alternative means of fragmenting the precursor molecules such as UV irradiation or thermal cracking. Reactive species from a source may flow directly to the substrate or may react with species (gas or radicals) from a separate source(s) so that resulting species have enhanced energy or reactivity with the photoresist and residues. Activation energy for the reactions on the substrate may be provided by ultraviolet light source illuminating the substrate and/or from chemical energy of the reaction products from a mixture of species from different sources flowing to the substrate. Specifically, radicals such as, for example, hydrogen atoms, oxygen atoms, NO, methyl radicals, sulfur oxide, hydroxyl, NH<sub>2</sub>, coming from one or more source(s), react with organic polymers or fluorinated organic polymers in the photoresist or residues. This permits stripping of substrates at commercially competitive rates at lower temperatures less than or about 150 or 200 Celsius instead of using thermal activation (  $\geq$  200 Celsius).
- The appropriate temperature should be selected as the highest temperature which essentially avoids temperature related damage, irrespective of the specific mechanism through with the damage arises. Because the reactive species MAT-P6

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may be generated in a (multiple) separate chamber(s), isolated from the substrate processing chamber, substrates are not exposed to the source of energy used for creation of the reactive species. This is because the source for radical generation may need to be so energetic that it could cause substrate damage with direct exposure. It is recognized herein that ultraviolet photons with energy of less than about 5 eV or chemical activation mechanism (for the removal of resist or conversion of residues) is gentle enough to avoid chemical damage to sensitive materials other than photoresist or photoresist residues at or near the substrate surface. If plasma use is undesirable, non-plasma sources may be used to provide radicals without simultaneous generation of charged particles. One such method uses photodissociation using energetic ultraviolet, such as from 172 nm excimer UV lamps, to dissociate molecular species such as, for example, O<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O, or other potential sources of desired reactive species and radicals.

¶23 In photoresist stripping for semiconductor fabrication, in order to promote reactions of radicals with the photoresist polymer and/or residues, it is necessary to provide energy to overcome the chemical "activation barrier" for oxidation of the polymer. One such reaction is:

(1) O + 
$$(CH)_n$$
  $\rightarrow$  CO + OH

¶24 In other cases, the activation energy may be higher – for instance when the photoresist has been "hardened" by exposure to intense ion bombardment during ion implantation doping of the silicon. In this case, the hydrogen content is substantially reduced and the linear carbon chains are substantially crosslinked so that the bonding becomes similar to that in graphite. In this case, the reaction with oxygen is:

$$(2) O + (C-C) \rightarrow CO$$

and the activation energy required to promote such reactions is greater than in equation (1). The energy required to break a carbon-carbon bond is about 3.7 eV. The latter reaction with atomic oxygen (or with atomic hydrogen) when activated thermally proceeds at a high rate when the substrate temperature is about 250 Celsius. However, this high a substrate temperature may also promote reactions of radicals with the sensitive dielectrics cited above or with dopants or impurities in crystalline silicon. Elevated temperature also promotes diffusion of oxygen and hydrogen atoms through such dielectrics that interfere with controlling the characteristics of the dielectric insulating layer. It is therefore desirable, in view of future process materials, to be able to remove photoresist at commercially acceptable rates while keeping the substrate at temperatures less than about 200 Celsius. The appropriate temperature should be selected as the highest temperature which, from a practical standpoint or at least to some approximation, avoids temperature related damage, irrespective of the specific mechanism through with the damage arises. In order to do this, an alternative source of activation energy for the stripping reaction must be provided.

Such alternative sources of activation energy include, but are not limited to ultraviolet photons, low energy electrons or ions. It is difficult, however, to provide electrons or ions with energies suitable for promoting such reactions as those contemplated herein for removing photoresist – that is, high enough to be effective, but not so high as to cause damage to the materials exposed on the surface. Therefore, ultraviolet photons with energies below the threshold for damage of the surface materials are considered by the present invention as a desirable form of activation energy, in some cases, to promote the reactions for stripping photoresist and residues. In other cases, the present invention contemplates

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providing energy to reactive radicals by reacting these radicals downstream from their source with one or more separately provided gas phase species.

In one embodiment of the present invention, ultraviolet radiation is used with photons of less than about 5 eV of energy to activate the chemical reactions of radicals with the photoresist to strip it while maintaining the substrate temperature at about 150 Celsius or less. In the case of some insulators, it may even be necessary to limit the photon energy to less than about 4 eV to avoid damage to the sensitive dielectric insulators or silicon. The ultraviolet activation is needed since the process temperature is below the temperature normally needed for removal of the photoresist or residues at a commercially acceptable rate. Such UV light may be provided by any suitable source including, but not limited to high pressure mercury lamps or excimer lamps or other sources such as plasma discharges where filtering of the light may be done to produce the desired spectrum of light for promoting the reactions while limiting/preventing damage to sensitive layers on the substrate surface. It is noted that the term "process related materials", as used in the appended claims, is intended to encompass photoresist and any residues related to the overall photoresist removal process. Such residues encompass reaction products of the photoresist with the process components such as, for example, process gases as well as reaction products between the process components and structures on the substrate. The residues may consist of mainly inorganic compounds formed as an overall polymeric bulk of a photoresist layer is stripped, generally using a dry process, by conversion to volatile compounds using oxygen or hydrogen radicals.

It should be noted that UV of 172 nanometer wavelength, which has been used in the prior art to promote reactions of oxygen or ozone with organic polymers on substrates, often has sufficient energy to cause damage to some sensitive dielectrics that are commonly used for semiconductor transistor fabrication. Annealing may be used to remove some kinds of damage caused to exposed materials, but this is not always the case. Since the threshold radiation for photodissociation of most molecules that can serve as sources for desirable radicals - such as hydrogen atoms, oxygen atoms, hydroxyl radicals - is above 5 eV, the present invention recognizes that it is highly advantageous to provide separate chambers for reactive species formation. That is, if this radiation could cause substrate damage, energy sources and chambers for creating reactive species should be separated from those promoting the reaction of radicals with the resist or residues. The usual energy that is needed for making some radicals by molecular dissociation using O<sub>2</sub>, NH<sub>3</sub> or H<sub>2</sub>O is about 6 eV, which means that it is usually necessary to have a separate source of radicals which is isolated from the process chamber in which the substrate is stripped of photoresist or residues. Other species such as NO<sub>2</sub> or H<sub>2</sub>CO may be dissociated by less energetic photons less than about 5 ev to produce the desired reactive species.

¶28 Table 1 summarizes the reference numbers that are used in the figures. It is noted that like reference numbers have been applied to like components, when possible, throughout the various figures.

TABLE 1

Ref. No.	Description
101	Substrate Processing Chamber
102	Substrate Holding Mechanism
103	Pins to Lift Substrate, 109, above the Substrate Support Surface, 104
104	Substrate Support Surface
105	Conduit to allow Reactive Species from Reactive Species Source, 106 or 116, to flow to Substrate Processing Chamber, 101

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106	Reactive Species Generator
107	Top Wall of Substrate Processing Chamber
108	Ultra Violet Energy Source, such as Mercury Lamps or
	Excimer Lamps or other Plasma based UV Energy Source
109	Substrate
110	Material to be removed from Substrate, 109, Surface such as
	Photoresist or Photoresist Residue
111	Ultra Violet Transparent Window to isolate Source of Ultra
	Violet Energy, 108, from Substrate Processing Chamber, 101, or from Reactive Species, 120.
	capable of eliminating certain high energy (short wavelength) photons that can cause damage
	to various aspects of the workpiece surface
112	Ultra Violet Transparent Showerhead Type Dispersion Plate to disperse Reactive Species,
	120 (120 and 121 if two Reactive Species Generators are used), capable of eliminating certain
	high energy (short wavelength) photons that can cause damage to various aspects of the
	workpiece surface
116	Reactive Species Generator
120	Reactive Species from Reactive Species Generator, 106
121	Reactive Species from Reactive Species Generator, 116
122	UV Reflective or UV absorbing or Short Wavelength UV Absorbing (for UV photons having
	wavelengths shorter than about 260 nm) Showerhead Type Dispersion Plate to disperse
	Reactive Species, 120 (120 and 121 if two Reactive Species Generators are used)
125	Conduit connecting two or more conduits, 105, to allow Reactive Species, 120 and 121, from
	Reactive Species Sources, 106 and 116, to combine and flow to Substrate Process Chamber,
	101
140	Ultra Violet Energy from Ultra Violet Energy Source
150	Exhaust Port for Process and Reaction Product Gases
200	Substrate Processing Reaction Zone

Attention is now directed to Figure 1 which illustrates a reactor system that is produced in accordance with the present invention. It is noted that terminology such as, for example, above, below, up, down, left and right, that is used with respect to the orientation and relative arrangements of items shown in the figures, is used only for purposes of descriptive clarity and is in no way intended as being limiting. Further, the drawings are diagrammatic in nature in order to enhance the readers comprehension and are not to scale. Moreover, the various components are not necessarily shown in relative scale with respect to one another. The system includes a substrate process chamber 101 from which gases may be continuously evacuated via an exhaust port 150 in any suitable manner such as those readily available in the prior art. Chamber 101 houses a substrate holding mechanism 102 which may include pins 103 that can elevate the substrate above a surface 104 and which may impart a regulated temperature, consistent with the aforedescribed appropriate process temperature. A reactive species 120 enters the chamber by an inlet or conduit 105, generally located near a top wall 107 of the substrate processing chamber, from a source of radicals – a reactive species generator 106. An ultraviolet energy source 108 illuminates substrate 109 with ultra violet energy 140 to activate the reactions of the reactive species with material 110 (photoresist or photoresist residue) to be removed from the surface of substrate 109.

¶30 A second embodiment of such a reactor system is shown in Figure 2. Figure 2 shows substrate processing chamber, 101, from which gases may be continuously evacuated via exhaust port 150 in any suitable manner such as those readily available in the prior art. In this embodiment, first and second sources 106 and 116, respectively, are provided which may be referred to as primary and secondary sources that provide first and second species indicated by the reference numbers 120 and 121. In one implementation, both sources comprise reactive species generators, having energy levels that are enhanced isolated from the substrate processing chamber, such that a first reactive species (as

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species 120), from first source 106 and a second reactive species (as species 121) from second generator 116 flow into the substrate processing chamber. In an alternative implementation, a first, isolatedly enhanced reactive species (as species 120), from first reactive species generator 106 is provided along with a gas or vapor (as second species 121) from second source 116, flowing into the substrate processing chamber. In this latter implementation, species 121, from gas or vapor source 116, then mixes with the reactive species from reactive species generator 106. The species from source 116 may react chemically to produce more energetic or reactive species to etch the photoresist or to form volatile or soluble forms of the photoresist residue. In any implementation, radicals from both sources 106 and 116 may also react synergistically with each other and photoresist 110 (as well as residues) on substrate 109 surface to remove the photoresist or to form volatile or soluble forms of the photoresist residue. Ultraviolet energy source 108 illuminates substrate 109 with ultraviolet energy 140 to activate reactions of the reactive species with the material to be removed 110 (photoresist or photoresist residue) on substrate 109 surface. Such a "downstream" energizing of radicals may be employed for resist or residue removal with or without use of the ultraviolet activation when the reaction rates for removal of photoresist or residue are adequate in the absence of such radiation.

- ¶31 A third embodiment of such a reactor system is shown in Figure 3. Figure 3 shows substrate processing chamber 101 from which gases may be continuously evacuated via exhaust port 150 in any suitable manner such as those readily available in the prior art. This embodiment resembles that of Figure 2 to the extent that first and second sources 106 and 116, respectively, are again provided. In this embodiment, however, sources 106 and 116 have their individual outflow conduits 105 connect to a common conduit 125, which then connects with substrate processing chamber 101. Again, reactive species may be provided from both sources or one source may provide gas or vapor species flowing into the substrate processing chamber. Accordingly, mixing of species 120 and 121 in conduit 105 may be advantageous since the species are afforded an additional reaction time with one another prior to entering the processing chamber. In this way, synergistic reactions may be even further enhanced. As above, the species from gas or vapor source 116 then mix with the reactive species from reactive species generator 106. The species from source 116 may react chemically to produce more energetic or reactive species to etch the photoresist or to form volatile or soluble forms of the photoresist residue. Radicals from both sources 106 and 116 may also react synergistically with each other and the photoresist 110 on substrate 109 surface to remove the photoresist or to form volatile or soluble forms of the photoresist residue. Ultraviolet energy source 108 illuminates substrate 109 with ultra violet energy 140 to activate reactions of the reactive species with material 110 (photoresist and/or photoresist residue) to be removed, on substrate 109 surface. Such a "downstream" energizing of radicals may be employed for resist or residue removal with or without use of the ultraviolet activation when the reaction rates for removal of photoresist or residue are adequate in the absence of such radiation.
- The reactor system shown in Figure 1 may be reconfigured in several ways that allow the maximum process benefits to be matched to the specific requirements of the photoresist material or photoresist residue to be removed and to minimize damage to sensitive materials on the surface of substrate 109, for example, by adding or reconfiguring the process chamber components. Possible embodiments are shown in Figures 4a through 4e.
- ¶33 In Figure 4a, the UV energy source is isolated from the reactive species and an isolated substrate processing environment 200 (or substrate processing chamber 101) by a UV transparent window 111. UV transparent window 111 may be selected to absorb or reflect UV photons having energy above a threshold known to cause damage to sensitive materials on the substrate surface.

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- In Figure 4b, a UV transparent showerhead type dispersion plate 112 is positioned above substrate 109 and below the UV energy source and the inlet of the reactive species. In this embodiment, dispersion plate 112, through which the reactive species are injected into processing environment 200, cause the reactive species to be dispersed so that the desired etch uniformity is maximized. Dispersion plate 112 may also be selected to eliminate UV photons with energies sufficiently high so as to cause damage to sensitive materials on the substrate. That is, the material for dispersion plate 112 may be selected so as to absorb or reflect UV photons having energy above a threshold known to cause damage to sensitive materials on the substrate surface.
- In Figure 4c, UV energy source 108 is isolated from the reactive species and the substrate processing environment 200 [or substrate processing chamber 101] by UV transparent window 111. UV transparent window 111 may be selected as to selectively eliminate UV photons with energies sufficiently high so as to cause damage to sensitive materials on the substrate or window 111 may be selected so as to promote additional activation of radical species introduced through conduit 105. UV transparent showerhead type dispersion plate 112 is positioned above substrate 109 and below the UV energy source and the inlet of the reactive species. In this embodiment, dispersion plate 112, through which the reactive species are injected into substrate processing environment 200, may be used to cause the reactive species to be dispersed so that the desired etch uniformity is maximized. Dispersion plate 112 may also be selected so as to eliminate UV photons with energies sufficiently high as to cause damage to sensitive materials on the substrate. That is, the material for dispersion plate 112 may be selected so as to absorb or reflect UV photons having energy above a threshold known to cause damage to sensitive materials on the substrate surface.
- In Figure 4d, UV energy source 108 is isolated from the reactive species and substrate processing environment 200 [or substrate processing chamber 101] by UV transparent window 111. UV transparent window 111 may again be selected as to selectively eliminate UV photons with energies sufficiently high so as to cause damage to sensitive materials on the substrate and/or may be selected so as to promote additional activation of radical species introduced through conduit 105. A showerhead type dispersion plate 122 is positioned above substrate 109 and below the UV energy source and the inlet of the reactive species. In this embodiment, dispersion plate 122 is used to cause the reactive species to be dispersed so that the desired etch uniformity is maximized. Dispersion plate 122 can additionally be selected so as to eliminate UV photons from reaching the surface of the substrate 109. That is, dispersion plate 122 can be selected so as to absorb or reflect UV photons and thus prevent UV photons from reaching the sensitive materials on the substrate surface.
- Turning to Figure 4e, it should be appreciated that this embodiment is similar to that of Figure 4d except that a two piece dispersion plate is used to block UV radiation that might damage sensitive surface(s) on the substrate. For example, two instances of dispersion plate 122 can either absorb the damaging UV radiation or it can reflect it. Reflection may be preferable as this would allow the reflected UV to excite more of the reactive species 120, resulting in higher efficiency of excitation of the reactive species produced by source 106. As shown in the figure, the apertures of each dispersion plate are offset with respect to those of the other dispersion plate.
- ¶38 It is to be understood that the component combinations seen in Figures 4a-4e are equally applicable with regard to Figures 2 and 3 for similar purposes. Moreover, the features described throughout the present application may be combined in any desired manner.

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- ¶39 In any of the foregoing embodiments, the showerhead dispersion plate or plates may be made of quartz or sapphire or other material transparent or selectively transparent to ultraviolet so that the UV energy source may be positioned above the showerhead dispersion plate and still illuminate the substrate. Moreover, any suitable configuration is contemplated within the scope of the present invention so long as UV radiation, that will not damage sensitive surfaces on the substrate, reaches the substrate surface. If desired, the UV can be blocked entirely from reaching the substrate, for example, by using a dual plate showerhead configuration as shown in Figure 4e.
- The UV energy source used for such ultraviolet activation may also produce visible and infrared radiation that can be used to provide heat energy to the substrate to elevate its temperature quickly when desired for example, when a hotter substrate temperature is desired for a later stage of the stripping process. In such an event, it is likely that the substrate would be supported on pins 103 during the ramp of substrate temperature so that the thermal response of the substrate would be less affected by conduction of heat to a pedestal, 104, below it.
- ¶41 This invention may use any source of species, radical or otherwise, for either the primary or secondary species source. Such a source may be an oven, a chemical reaction chamber or chamber in which flowing gas is exposed to ultraviolet radiation capable of dissociating that gas, or a plasma discharge. Such sources have been diagrammatically illustrated since it is considered that they may readily be implemented by one having ordinary skill in the art in view of this overall disclosure. In using any of these sources, there may be a filter, grid or baffle employed in the duct leading to the substrate processing chamber which removes charged particles and/or undesired reactive species. This may be needed since sources may sometimes produce a variety of dissociation products from molecular feed gases while only certain of such products may be desired for stripping of the photoresist. One such example, when using ammonia gas, the amine radicals, NH2 produced along with hydrogen atoms by dissociation may not be desirable and so baffles may be used to cause them to be collected and prevent them from reaching the substrate processing chamber. As another example, when using methane to produce hydrogen atoms and methyl radicals, either species may not be desired and can be filtered out by an appropriate baffle. Surfaces that recombine hydrogen atoms such as, for example, aluminum, may be used as baffles. Alternatively, surfaces coated with Teflon (PTFE) may be used, which preserves hydrogen atoms. Surfaces such as quartz or sapphire may also be used since they cause charged particles and some neutral species to recombine.
- Hydrogen atoms or radicals containing hydrogen may be a preferred species for stripping photoresist and residues when photoresists contain fluorine. Hydrogen atoms have been shown to have reasonable etching rates for organic polymers at temperatures of 200 C and higher. Atomic hydrogen has a strong tendency to form gas phase HF when it chemically reacts with fluorinated materials. Anhydrous HF produced by that reaction is much less reactive with silicon and silicon-based dielectrics than is atomic fluorine. The use of ultraviolet has the capability to activate chemical reaction of hydrogen with both carbon polymers and fluorocarbon polymers, even at temperatures below 200 Celius. It is important that such UV radiation not cause un-annealable damage to the dielectric or promote undesired chemical reactions. It may therefore be necessary to restrict the energy of the ultraviolet to be less than that which causes etching of the dielectric or damage to it. This can be done, for example, by using a window for the UV energy source which absorbs ultraviolet that would be undesirable. For example, various composition glasses (such as those made by Corning glass) can easily absorb all ultraviolet with wavelengths below 250 to 300 nanometers, as desired. For example, Corning

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type 9700 glass stops all light below 250 nanometers while passing almost all light with wavelengths greater than 300 nanometers.

- Generally, the gas pressure in the radical source(s) may be in the range from tens of milliTorr to atmospheric pressure. When sources are meant to deliver oxygen atoms, the upper pressure limit may be about 2 to 100 Torr. Flows of gases are typically in the range from ten standard cubic centimeters per minute to approximately a few tens of liters per minute. The power delivered by the plasma source to dissociate radicals may be from a few hundreds of watts to several kilowatts. The ultraviolet power delivered to the substrate surface for activation may be in the range between about a hundred watts and about several kW. The ultraviolet power used in a radical source for dissociation of species may be in the range between about a few tens of watts and about a kiloWatt.
- Materials that may be used generally as feedstock into the radical sources include, but are not limited to: water vapor, ammonia, carbon dioxide, nitrogen dioxide, nitrogen monoxide, formaldehyde, methyl or ethyl alcohol, methylamine, nitrosomethane, ethane, methane, nitrosoformaldehyde, formic acid, sulfur dioxide, nitrous oxide, and other compounds of oxygen, hydrogen, carbon and nitrogen which have substantial vapor pressures at or below 150 Celsius and which may serve after fragmentation as sources of radicals such as hydroxyl, nitrogen oxide, hydrogen atoms, oxygen atoms.
- ¶45 Examples of configuration, gas mixtures and modes of activation that may be used in different cases and each of which is readily implemented in view of the foregoing descriptions:
- Oxygen gas is dissociated in the First Radical Source by a UV source with wavelength of about 172 nanometers to produce oxygen atoms. Oxygen atoms injected to substrate process region via a showerhead made of quartz (or sapphire coated quartz). An ultraviolet source illuminates the substrate with between about a few tens of watts and about a few hundred Watts of ultraviolet radiation above about 250 nm in wavelength to activate reactions on the substrate with photoresist. The substrate is supported on a pedestal with temperature held between about 20 Celsius and 150 Celsius for at least one step of the stripping and/or residue removal process.
- Oxygen gas is dissociated in the First Radical Source by a UV source with wavelength of about 172 nanometers to produce oxygen atoms at pressures between about 10 milliTorr and about 10 Torr. Oxygen atoms introduced by showerhead with a second injected gas being a hydrocarbon such as methane which may be mixed in dilute mixture with an inert gas such as argon or helium. Substrate supported on a pedestal at a temperature between room temperature and about 150 Celsius.
- Oxygen gas injected into a first radical source at a flow of between about 100 standard cc per minute and about 10 standard liters per minute dissociated by a plasma source and introduced by a showerhead to the substrate process region at a pressure of between about 0.2 Torr and about 10 Torr. Ammonia gas is dissociated in a second radical source by ultraviolet lamps at about 172 nanometers introduced by a second injector as in Figure 3 at a flow between about 10% and 100% of the oxygen flow. No ultraviolet illumination of the substrate is used for activation.
- Nitrogen dioxide gas is injected into a first radical source. This is dissociated into NO and O by a UV source providing from about a few tens of Watts to about a kilowatt of radiation in the wavelength band. The radicals from the MAT-P6

first source are mixed in the substrate process region with ammonia gas from a second source as in Figure 3. The streams from the two sources react chemically to provide a heated gas stream containing NO, OH and other species. Flow of nitrogen dioxide is in the range from about 100 standard cc per minute to about 5 liters per minute, and the flow of ammonia is between about 5% and 100% of nitrogen dioxide flow.

- ¶50 A first source of radicals uses ammonia gas at a flow of about 100 to 10,000 standard cc per minute. This is dissociated in the radical source into NHx and H atoms by a about 172 nm ultraviolet light source. The second source using oxygen atoms dissociated by ultraviolet light at about 172 nanometers. Gases are injected into the substrate region at a pressure of less than about 10 Torr to form radicals such as NO, OH, H and O.
- Methyl alcohol is dissociated by ultraviolet light into methyl and hydroxyl radicals from a first source injected into the chamber with oxygen radicals from a plasma source. Result is a highly energized mixture of partial combustion products of methyl radicals and oxygen as well as hydroxyl radicals. Pressure is less than about 10 Torr. The flow of alcohol is less than about two liters per minute while the oxygen flow may be from about 10% of the alcohol flow to about twice the alcohol flow.
- A first source of radicals is injected with formaldehyde at a flow between about several hundred standard cc per minute and about ten standard liters per minute. The gas is dissociated into hydrogen atoms and carbon monoxide by about several tens of Watts to one kilowatt of ultraviolet light with wavelength less than about 270 nanometers. The radicals are introduced into the substrate process region through a showerhead dispersion plate such as in Figures 4b, 4c and 4d where between about several tens of watts and about one kilowatt of ultraviolet light, in the wavelength region greater than about 300 nanometers, illuminates the substrate and promotes reaction of radicals with the photoresist or residues on the substrate. The pressure in the substrate process chamber may be from about 0.1Torr to about 100 Torr.
- Although each of the aforedescribed physical embodiments have been illustrated with various components having particular respective orientations, it should be understood that the present invention may take on a variety of specific configurations with the various components being located in a wide variety of positions and mutual orientations. Furthermore, the methods described herein may be modified in an unlimited number of ways, for example, by reordering, modifying and recombining the various steps. Accordingly, it should be apparent that the arrangements and associated methods disclosed herein may be provided in a variety of different configurations and modified in an unlimited number of different ways, and that the present invention may be embodied in many other specific forms without departing from the spirit or scope of the invention. Therefore, the present examples and methods are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein, but may be modified at least within the scope of the appended claims.

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